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HEAT RELEASE KINETICS

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A molecular basis for polymer burning is developed from thermal degradation kinetics and compared to experimental data for flaming heat release rate in fires. The solid-state fuel generation rate in fires has been derived [1] from the polymer thermal degradation scheme

Gas, G

Δ $\uparrow$

Polymer, P $\underset{\leftarrow}{\rightarrow}$ Reactive Intermediate, I*

$\downarrow$
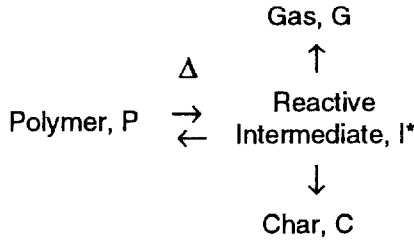
Char, C

assuming that the majority of pyrolysis gases G and char C are produced anaerobically from the reactive intermediate I* in a single step via parallel reactions. The system of rate equations for the species at time, t, is

$$\frac{dP}{dt} = -k_p P + k_{-p} I* \tag{1}$$

$$\frac{dI*}{dt} = k_p P - \left(k_{-p} + k_g + k_c\right) I* \tag{2}$$

$$\frac{dG}{dt} = k_g I* \tag{3}$$

$$\frac{dC}{dt} = k_c I* \tag{4}$$

The stationary-state assumption $dI*/dt \approx 0$ eliminates I* from Equations 1-4. Defining an initial mass, $m_0 = P + G + C + I* \approx P + G + C$, and a sensible mass, $m = P + C + I* \approx P + C$, the maximum fractional mass loss rate at a constant heating rate $\beta = dT/dt$ is

$$\frac{\dot{m}_{max}}{m_o} = \frac{-\beta(1-\mu)E_a}{eRT_p^2} \tag{5}$$

where E_a is the molar activation energy for the rate limiting $P \rightarrow I*$ decomposition step, $\mu = C(\infty)/m_o$ is the equilibrium char fraction at the peak mass loss rate temperature, T_p, R is the gas constant, and e is the natural number. Multiplying Equation 5 by the heat of complete combustion of the pyrolysis gases h_c^o gives the *kinetic heat release rate*

$$\dot{Q}_c(W/kg) = h_c^o \frac{-\dot{m}_{max}}{m_o} = \frac{h_c^o \beta(1-\mu)E_a}{eRT_p^2} \tag{6}$$

The pyrolysis zone thickness for steady burning of a polymer of thermal conductivity κ at net surface heat flux $\dot{q}_{net}$ is

$$\delta = \frac{e\kappa}{\dot{q}_{net}} \frac{RT_p^2}{E_a} \tag{7}$$

The areal density of pyrolyzing polymer of bulk density ρ and surface area S is $m_0/S = \rho\delta$ so that the macroscopic heat release rate per unit area of burning surface is

$$\dot{q}_c(W/m^2) = \chi h_c^o \frac{\dot{m}}{S} = \chi\rho\delta \left[h_c^o \frac{\dot{m}}{m_o}\right] \tag{8}$$

or with Equation 6

$$\dot{q}_c = \chi\rho\delta \dot{Q}_c \tag{9}$$

Equation 9 states that the ratio of the steady-state macroscopic heat release rate to the peak kinetic heat release rate for comparable temperature histories is in the range

$$\frac{\dot{q}_c}{\dot{Q}_c} = \chi\rho\delta \approx 0.4 \pm 0.2 \, kg/m^2 \tag{10}$$

using typical values for the gas phase combustion efficiency in a fire, $\chi = 0.7 \pm 0.2$, the polymer density, $\rho = 1000 \pm 100$ kg/m^3, and the pyrolysis zone thickness, $\delta = 0.5 \pm 0.2$ mm at $\dot{q}_{net} = 50$ kW/m^2 from Equation 7.

The heating rate at the surface of a steadily burning polymer is

$$\beta = \left.\frac{dT}{dt}\right|_{x=0} = \frac{\dot{q}_{net}^2}{\kappa \rho c_p (T_p - T_o)} \qquad (11)$$

with $c_p = c(T_p)$ the polymer heat capacity at the peak pyrolysis temperature. Substituting Equation 11 along with Equations 6 and 7 into Equation 9 recovers the continuum result for thermal diffusion limited steady burning

$$\dot{q}_c (W/m^2) = \chi h_c^o \frac{\dot{m}}{S} = \chi \frac{h_c^o}{h_g} \dot{q}_{net} \qquad (12)$$

with the heat of gasification defined $h_g \equiv c_p(T_p - T_o)/(1-\mu) = \dot{q}_{net}/(\dot{m}/S)$.
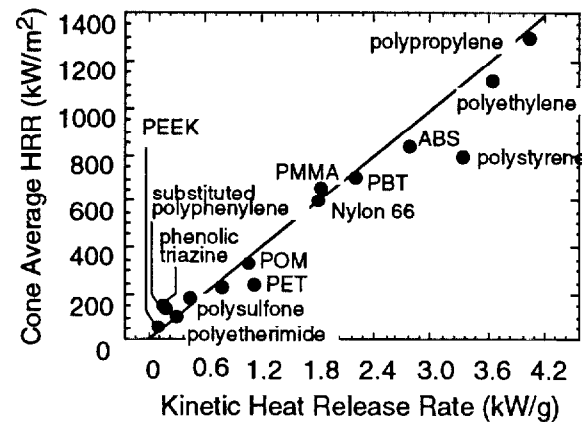
In principle the macroscopic heat release rate at any net surface heat flux $\dot{q}_{net}$ is now calculable from the pyrolysis kinetic parameters and heat of combustion of the volatiles using Equations 6, 7, 9, and 11. However, these kinetic and combustion parameters are rarely known with any certainty, particularly at the surface heating rates in a fire.

Consequently, our approach [2] was to measure the kinetic heat release rate directly using pyrolysis-combustion flow calorimetry (PCFC). In the PCFC test a 1-3 milligram polymer sample is pyrolyzed by heating in an inert environment to a maximum temperature $T_{max} = 923$K at a linear heating rate $\beta \approx 8$ K/s (calculated from Equation 11) to approximate the rapid, anaerobic heating of a polymer surface in a fire or fire calorimeter at $\dot{q}_{net} = 50$ kW/m^2.

The pyrolysis gases are swept from the small volume pyrolysis chamber of the PCFC by flowing nitrogen and mixed with excess oxygen prior to entering a 900°C furnace to effect complete combustion. Combustion products are scrubbed from the gas stream

prior to entering an oxygen analyzer. Heat release rate is calculated from oxygen consumption and the measured flow rate of the gas stream.

Results of these PCFC tests are compared to literature values for average macroscopic heat release rate at $\dot{q}_{net} = 50$ kW/m^2 in a cone calorimeter in the figure below.

Macroscopic *versus* kinetic heat release rate for some polymers.

Proportionality is observed between the macroscopic and kinetic heat release rates with slope $\dot{q}_c / \dot{Q}_c = 0.33$ kg/m^2, which is within the range of predicted values using Equation 10.

We conclude that steady polymer burning is a thermal diffusion controlled kinetic process in which the rates of the solid-state reactions (pyrolysis) and gas phase reactions (combustion) are rapid in comparison to the rate of heat transfer at the flaming surface. The pyrolysis zone depth is determined by the coupling between thermal diffusion and pyrolysis kinetics and effectively correlates the molecular and macroscopic heat release rates.

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